High Thermal Conductivity Epoxy Molding Compound Filled with a Combustion Synthesized AlN Powder

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ABSTRACT: A combustion synthesized AlN powder was studied for its feasibility as a filler for epoxy molding compound (EMC) and effects of various experimental parameters on the thermal conductivity and moisture resistance of the EMC were investigated. The AlN powder was coated with silane both to increase the moisture resistance of the EMC and to enhance the bonding between the filler AlN and the matrix resin. The thermal conductivity could be significantly increased by using AlN powders with large particle sizes and this was considered to be due to a reduction in interface area between the AlN particles and the matrix resin. A thermal conductivity of 14 W/mK was obtained when the EMC was fabricated by a process involving no use of a solvent and a AlN powder with a particle size of 35.3 μm and a filler content of 67 vol % were used. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4734–4740, 2006

Key words: aluminum nitride (AlN); self-propagating high temperature synthesis (SHS); epoxy molding compound (EMC); thermal conductivity

INTRODUCTION

As the development of chips toward higher density and higher frequency, more and more waste heat must be removed to make the chips stable. The traditional epoxy molding compound (EMC), which uses silica as filler, cannot meet the requirement of high-thermal-conduction encapsulation[1] because the thermal conductivities of epoxy and silica are both low (epoxy – 0.15–0.25 W/mK,[2,3] and silica – 1.3–14 W/mK[4]). In general applications, silica has been widely used as filler mainly because it is low in cost and the relevant application techniques have been well developed. An effective and feasible way to increase the thermal conductivity of EMC is to use a high-thermal-conductivity ceramic material as filler and to develop the relevant application techniques.[5]

Among various ceramic materials, aluminum nitride has been considered as an ideal candidate for EMC filler because of its unique combination of many desirable properties such as high thermal conductivity (theoretical value 320 W/mK), high electrical resistivity ($> 10^{14}$ Ω cm), low thermal expansion coefficient (theoretical value 4.4 ppm/°C), and moderately low dielectric constant (8.7–8.9 RT – 1 MHz).[6–8] Recently, AlN-filled EMC has been the research subject of many studies.[4,9–11] A thermal conductivity of 10 W/mK or higher has been reported for the AlN-filled EMC.[9,11]

In practical applications, however, high market prices have been hindering the use of AlN as the filler for EMC. In addition, many relevant technical problems concerning the fabrication and use of EMC are yet to be solved. A significant problem is the high reactivity of AlN with moisture. Reaction of AlN with moisture will cause the formation of $Al(OH)_3$ and NH_3, which will damage the circuit and the EMC itself. One other problem is the poor affinity of AlN with the resin matrix, which forms a great thermal conduction resistance at the interface, and thus causes a significant reduction in thermal conductivity of the EMC.

In our previous studies,[12–15] a SHS (self-propagating high temperature synthesis or combustion synthesis) process has been developed for synthesis of AlN, which is characterized by simple processing, low energy consumption, fast production rate, high purity of product, and low production cost. It is thus interesting to study the feasibility of using the AlN powder (synthesized by the SHS process developed in our previous studies) as filler for EMC. In fact, this is one of the objectives of the present study. The other objective of the present study is to investigate the effects of many important experimental parameters such as silane coating, filler content, and particle size on the thermal conductivity and moisture resistance of EMC.

EXPERIMENTAL

The AlN powder used in the present study was prepared by our newly developed combustion synthesis

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TABLE I
Characteristics of the As-Synthesized and the Ground AlN

Type of AlN	Average particle size D_{50} (μm)	Specific surface area (m^2/g)	Oxygen content (wt %)
As-synthesized	–	–	0.22
Powder A	2.3	2.7	1.51
Powder B	4.5	1.4	1.01
Powder C	6.3	0.6	0.64
Powder D	14.3	0.2	0.49
Powder E	19.0	0.1	0.41
Powder F	25.3	(0.088)[a]	0.39
Powder G	29.2	(0.087)[a]	0.36
Powder H	35.3	(0.087)[a]	0.26

[a] Obtained by calculation assuming spherical particles.

method.[13–15] To investigate the effect of particle size of the AlN powder on the thermal conductivity of EMC, the as-synthesized AlN product was crushed to under 60 mesh and then attrition milled to specific particle sizes, using AlN balls (diameter 5 mm) with high purity acetone (99.9%) as the milling fluid. The characteristics of the as-synthesized and the ground AlN are listed in Table I. Since smaller particle sizes were obtained with longer grinding times, which cause higher oxygen contents, the oxygen content of the AlN powder (Table I) increases with decreasing particle size. To avoid higher oxygen contents in the AlN powder, the smallest particle size tested in the present study was arbitrarily chosen to be 2.3 μm. Since too big particle size often causes problems in applications (e.g., surface roughness and scratching the die surface), the largest particle size tested in the present study was arbitrarily chosen to be 35.3 μm. All the ground AlN powders are irregular in shape, as shown in Figure 1.

Because of high affinity and reactivity of AlN powder to moisture and water,[16] a surface treatment process was undertaken to prevent the AlN powders from hydrolyzing. 3-Aminopropyl-triethoxy silane (aminosilane), was used as the surface treatment agent. The AlN powder and an appropriate amount of the silane (0.5–1 wt % based on the weight of AlN powder) were mixed in high purity acetone by stirring for at least 3 h. The slurry was filtered and then dried in a vacuum oven at 120°C for 1 h. A surface-treated AlN powder was thus obtained. The surface treatment agent also serves as coupling agent,[17] which enhances the bonding between the AlN particles and the epoxy resin matrix because the silane has two different functional groups of which one is reactive with the epoxy resin and the other reacts with the surface of the AlN particles.

Listed in Table II are the components and their percentage contents used to prepare the EMC specimens in the present study. (The percentage content is defined as the weight percent of each component based on the total weight of the EMC specimen except that of the coupling agent, which is based on the weight of the AlN powder.) Cresol novalac epoxy resin (CNE) and phenol novalac (PN) were used as the epoxy resin matrix and the hardener, respectively. Triphenyl phosphine (TPP) was used as catalyst in the initial stage of the study, and in the later stage, 1-benzyl-2-methylimidazole was used.

In the initial stage of the study, the EMC specimens were fabricated by following a process developed and used in many other studies[18,19] which involves the use of a solvent. In this process, the epoxy resin, the hardener, and the TPP catalyst were dissolved in high purity acetone and then mixed thoroughly with the surface-treated AlN powder by stirring for at least 3 h. After mixing, the slurry was dried in a vacuum oven at 80°C and the dried product was then crushed to obtain a powder under 12 mesh. The EMC specimen was obtained by transfer molding the powder at 175°C and 50 kg/cm^3 for 5 min, and finally, the specimen was placed in a vacuum oven at 180°C for 6 h for postcuring to obtain a higher degree of crosslinking. (This process for fabricating EMC specimens will be referred to as Process I.)

A process involving no use of a solvent was also developed in the present study for fabrication of the EMC specimens. In this process (will be referred to as Process II), CNE and PN were used as the epoxy resin and the hardener, respectively. They were mixed thoroughly by heating them to a liquid state at 100°C with simultaneous stirring. The surface-treated AlN powder was then added to the liquid and the mixture was further heated to 150°C with simultaneous stirring for at least 15 min to obtain a good dispersion of the AlN

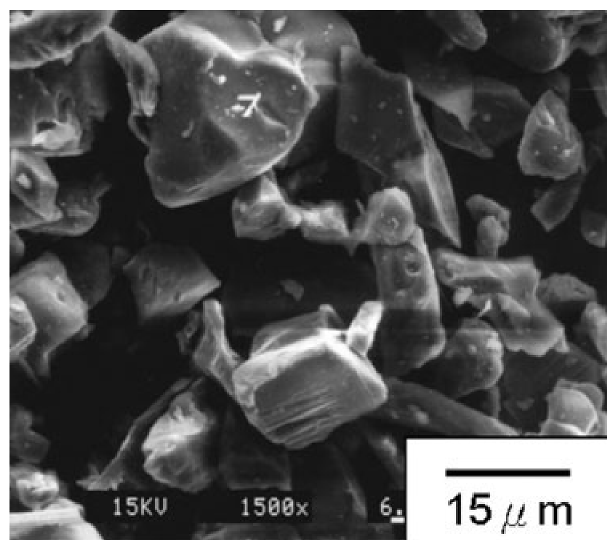

Figure 1 A typical SEM photograph of the ground AlN powder (powder D).

TABLE II
Components and their percentage contents of EMC specimens

Component (function)	Compound or commercial name of component	Physical state at room temp.	Percentage contents (wt%)[a]
Filler[b]	Surface-treated AlN powder	Solid	60–85
Matrix	Cresol novolac epoxy resin (CNE)	Solid	5–30
Hardener	Phenol novolac (PN)	Solid	2.5–10
Catalyst	Triphenyl phosphine (TPP) or 1-benzyl-2-methylimidazole	Solid/liquid	0.1–0.5/0.1–0.5
Coupling agent	3-Aminopropyl-triethoxy Silane	Liquid	0–5

[a] The wt % of the coupling agent is based on the weight of the AlN powder but others are based on the weight of the EMC specimen.
[b] The filler content expressed as volume percentage of AlN in the EMC specimen.

particles in the liquid. To assure a good contact between the catalyst and the mixture and to prevent crosslinking from occurring at this stage, a liquid catalyst, i.e., 1-benzyl-2-methylimidazole, was used and it was added gradually to the mixture with simultaneous stirring during the period of cooling of the mixture. After cooling, the product was crushed to under 12 mesh and the EMC specimens were obtained by transfer molding under the same conditions as in Process I. Shown in Figure 2 is a flow sheet illustrating the two processes.

The particle size distribution and the oxygen content of the AlN powder were measured by a centrifugal-sedimentation particle size analyzer (Brookhaven, BI-XDC, USA) and a N/O analyzer (LECO, TC 300, USA), respectively. The specific surface area of the AlN powder was measured using a BET surface area analyzer (Quantachrome, NOVA 1000e). However, for those powders with large particle sizes (i.e., powders F, G, and H), their specific surface areas were obtained by calculation assuming spherical shape because they were difficult to be measured by the BET surface area analyzer. The densities of the EMC specimens were measured by an Archimedes displacement method and moisture absorptions of the specimens were measured by using a humidity test chamber (Terchy, Taiwan) at 85°C and 85% RH (relative humidity). The thermal diffusivities and heat capacities of the specimens were measured by a laser flash method (NETZCH, Microflash 300, Germany). The thermal conductivities of the specimens were then obtained by calculation according to the formula:[20] $K = C_p\rho\alpha$, where K is thermal conductivity, C_p is the heat capacity, ρ is the density, and α is the thermal diffusivity.

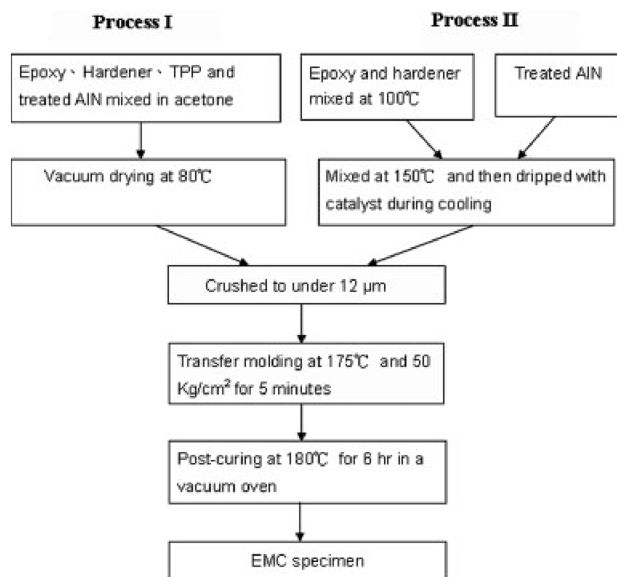

Figure 2 The two different processes for fabrication of the EMC specimens.

RESULTS

Process I

Effects of filler content and silane coating

Figure 3 shows the effects of filler content and silane coating on the thermal diffusivity and the thermal conductivity of the EMC specimens fabricated by Process I. (The filler content is defined as the volume per-

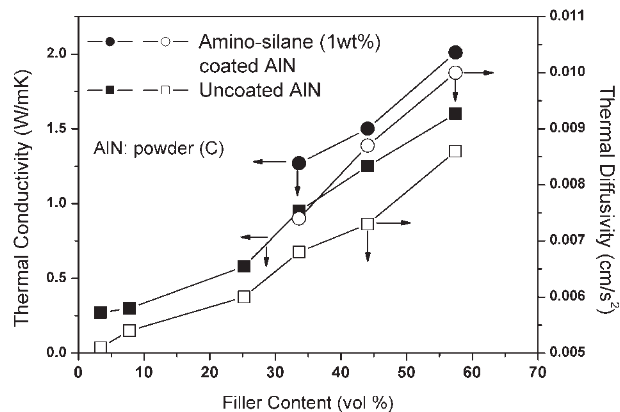

Figure 3 Effects of filler content and silane coating on thermal diffusivity and thermal conductivity of EMC.

centage of the AlN powder in the EMC specimen.) The filler used was AlN powder C, which had an average particle size of 6.3 μm and an oxygen content of 0.64 wt % (Table I). As can be seen, both the thermal diffusivity and the thermal conductivity of the EMC specimens increase with increasing filler content in either case where the AlN powder was coated with aminosilane (1 wt %) or without coating. However, at the same filler content, both the thermal diffusivity and the thermal conductivity were significantly higher with silane coating. At a filler content of 57 vol %, the thermal conductivity of the specimen filled with uncoated AlN is 1.5 W/mK and that of the specimen filled with coated AlN reaches 2 W/mK. (Both densities and the heat capacities of the specimens filled with silane-coated AlN are only slightly higher than those of the specimens filled with uncoated AlN and their differences are less than 2 and 3%, respectively.)

Figure 4 shows the effect of the amount of silane used in AlN coating on the thermal conductivity of EMC where the filler content was kept constant at 50 vol %. As can be seen, within the range tested (i.e., 0–5 wt %), silane coatings all increased the thermal conductivity of the EMC specimens and the maximum thermal conductivity was obtained at 1 wt % of silane used. In the subsequent experiments, 1 wt % of silane was thus used in coating the AlN powders.

Moisture resistance of specimen

Figure 5 shows the effects of silane coating and testing time on moisture absorption of the EMC specimens in an environment of 85°C and 85% RH. (The moisture absorption, which is a measure of the amount of moisture absorbed by the EMC specimen, is expressed as the percentage of the weight increase of the specimen.) As can be seen, the specimen filled with uncoated AlN increases in weight with increasing time and reaches 0.8 wt % after a testing time of 144 h. The specimens filled with 1 or 3 wt % silane-coated AlN absorb much less moisture than those filled with uncoated AlN after a long testing time (i.e., 144 h). The specimen filled with 1 wt % silane-coated AlN absorbs more moisture than that filled with 3 wt % silane-coated AlN at short testing times (i.e., < 100 h). After a long testing time (i.e., > 120 h), however, it seems to stop absorbing and its moisture absorption is very close to that of the specimen filled with 3 wt % silane-coated AlN.

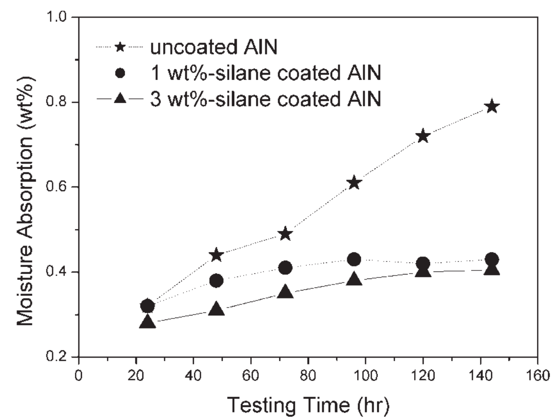

Figure 5 Effects of silane coating and testing time on moisture absorption of EMC.

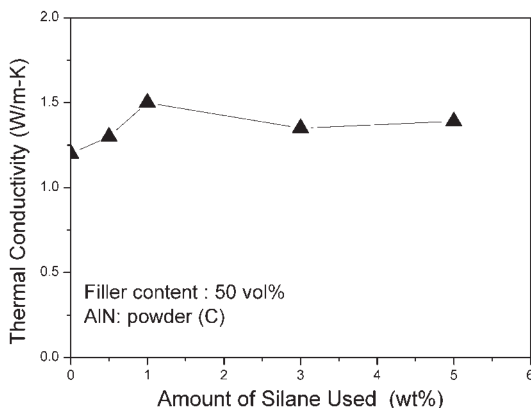

Figure 4 Effect of amount of silane used in AlN coating on thermal conductivity of EMC.

Process II

Figure 6 shows the effects of filler content on the thermal diffusivity, the thermal conductivity and the density of the specimens filled with 1 wt % silane-coated AlN and fabricated by Process II. For comparison, similar results for the specimens filled with the same type of coated AlN but fabricated by Process I are also shown in this figure. As can be seen, except at the filler content of 33 vol %, the thermal diffusivities, the thermal conductivities, and the densities of the speci-

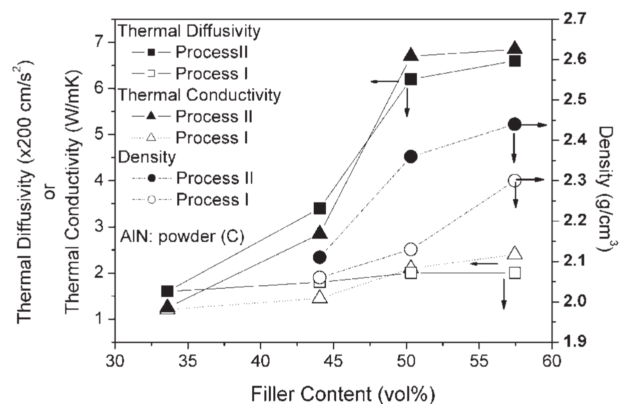

Figure 6 Effect of filler content on thermal diffusivity, thermal conductivity, and density of the EMC specimens fabricated by Process II. Similar results for the specimens fabricated by Process I are also shown for comparison.

mens fabricated by Process II are all significantly higher than those obtained by Process I. For the thermal diffusivity and the thermal conductivity of the specimens fabricated by Process II, they both increase significantly as the filler content increases from 33 to 50 vol %, but increase only slightly as the filler content is further increased from 50 to 57 vol %. (The heat capacities of the specimens fabricated by Process II are only slightly higher than that of the specimens fabricated by Process I and their difference is less than 3%.)

Effect of particle size

Shown in Figure 7 is the effect of particle size of the AlN powder on the thermal conductivity of the EMC specimens fabricated by Process II. The specific surface areas of the AlN powders (equivalent to the interface surface area per gram of filler) are also shown in this figure. In these experiments, the filler content was kept constant at 50 vol % and the AlN powders were all coated using 1 wt % of silane solution. The thermal conductivity is seen to increase significantly with increasing particle size and to reach 11 W/mK at a particle size of 35.3 μm.

Shown in Figure 8 is the effect of the filler content on the thermal conductivity when the AlN powder with a particle size of 35.3 μm (i.e., powder H) is used. For comparison, similar results using the AlN powder with a particle size of 6.3 μm (i.e., powder C) are also shown in this figure. All the AlN powders were coated using 1 wt % of silane solution and the EMC specimens were all fabricated by Process II. In the case of using AlN powder H, the thermal conductivity increases abruptly as the filler content increases from 33 to 45 vol %. The thermal conductivity continues to increase with increasing filler content and reaches 14 W/mK when the filler content is 67 vol %. The thermal conductivities of the specimens filled with AlN powder H (35.3 μm) are seen to be much higher than those filled with AlN powder C (6.3 μm) when the filler content is increased to or beyond 45 vol %. The dependence of thermal conductivity on filler content as predicted by Kanari equation is also shown in Figure 8 and will be discussed in the following section.

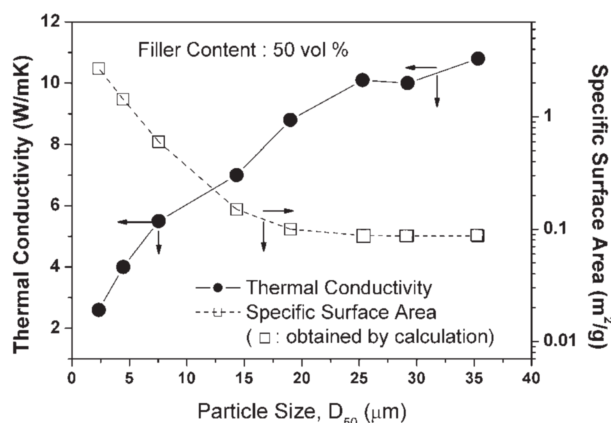

Figure 7 Effect of particle size of the AlN powder on thermal conductivity of the EMC specimens fabricated by Process II. The specific surface areas of the powders are also shown.

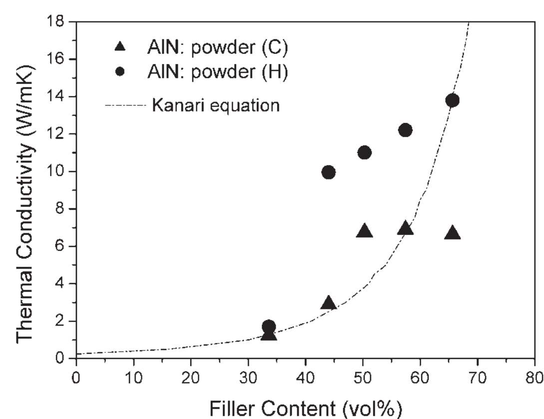

Figure 8 Effect of filler content on thermal conductivity of the EMC specimens filled with either powder C or H of the AlN.

DISCUSSION

As pointed out by other investigators,[4,9–11] to increase the thermal conductivity of EMC filled with particulate AlN, it is essential to minimize the thermal conduction resistance associated with the interfaces between the filler and the matrix. To reduce the thermal conduction resistance associated with the interfaces, two approaches can be undertaken, namely, to reduce the amount (or the area) of the interfaces, and to reduce the thermal conduction resistance at the interfaces. The amount of interfaces can be reduced by using a filler with larger particle sizes. To reduce the thermal conduction resistance at the interfaces, it has been suggested and tested[11] to coat the AlN particles with a coupling agent (e.g., silane), which can enhance the bonding between the filler and the matrix. The results of the present study clearly show the effects of AlN particle size and silane coating on the thermal conductivity of EMC. In addition, the importance of developing a proper process for the fabrication of EMC with a high density is also shown in the present study.

Silane coating

It is believed[16,21] that hydroxyl groups exist on the surface of AlN particles acting as bases and these hydroxyl groups can accelerate the hydrolysis of AlN particles. Silane can hydrolyze in aqueous solution (including the acetone as used in the present study in

which a small amount of water is contained) and its ethoxy groups will transform to hydroxyl groups.[17] It has been suggested[22] that these hydroxyl groups serve as acids and react with the hydroxyl groups on the surface of the AlN particles. This was also supported by the authors' previous study[23] in which the functional groups of silane were detected by XPS (X-ray photoelectron spectroscopy, ESCA210, VG) on the surface of the silane-coated AlN powder. Besides, water resistance of the silane-coated AlN powder was significantly enhanced, which was best explained by formation of chemical bonding between silane and the AlN particles.

While the hydroxyl groups of silane react with that of the AlN particles, the amino groups at the other ends of silane can react with the epoxy during the curing process. The thermal conduction resistance is thus reduced by silane coating because the bonding between the AlN filler and the epoxy matrix is enhanced. The thermal conductivity of the EMC specimen is therefore increased as the AlN powder is coated with silane (see Fig. 3 and note that in the case, the effects of density and heat capacity on the thermal conductivity are both negligible because their variations are less than 2 and 3%, respectively.). As mentioned previously, the hydroxyl groups on the surface of the AlN particles can accelerate the hydrolysis reaction of the AlN particles and silane will react with these hydroxyl groups. The moisture absorption of the EMC specimen filled with silane-coated AlN is thus reduced (see Fig. 5), because the amount of the hydroxyl groups on the AlN particles is reduced by the silane coating.

Processing methods

As can be seen in Figure 6, the specimens fabricated by Process I have lower densities and lower thermal conductivities than those fabricated by Process II. It was suspected that the solvent (i.e., acetone) used in the mixing step of Process I (see Fig. 2) might be responsible for the low densities and low thermal conductivities due to evaporation of the solvent during the vacuum drying step thus forming pores and barriers to thermal conduction. A certain extent of crosslinking might also take place in the matrix during the vacuum drying step because the materials were maintained at 80°C for several hours with the presence of catalyst during vacuum drying. These pores were thus difficult to be eliminated in the subsequent step of transfer molding because the crosslinked resin could not move freely to fill the pore spaces. Low densities (or high volumes of pores) of the specimens can decrease the thermal conductivity by three ways, namely by directly decreasing it and by decreasing the heat capacity and the thermal diffusivity. (Note that $K = C_p\rho\alpha$) As mentioned previously, the difference in heat capacity between the specimens fabricated by Process I and II is small (<3%) and its effect is negligible. However, the effects of the density itself and the thermal diffusivity are obvious. These can be seen clearly in Figure 6 where the densities and the thermal diffusivities obtained by Process I were both significantly lower than those obtained by Process II. The thermal conductivity of the specimens fabricated by Process II was thus higher than that of the specimens fabricated by Process I.

Filler particle size and filler content

As mentioned previously, the thermal conductivity of EMC can be increased by using a filler with large particle sizes because the interface area between the filler and the matrix resin decreases with increasing particle size (under the condition that the filler content is kept constant). Such a particle size effect is seen clearly in Figure 7. In fact the increase in thermal conductivity shown in Figure 7 may be partially due to the decrease in oxygen content of the AlN powder as its particle size increases. (See Table I and note that the thermal conductivity of AlN increases with decreasing oxygen content.) However, within the range of the oxygen content of the AlN powders used in the present study (0.26–1.51 wt %), the variation in thermal conductivity of the AlN powder is expected to be not greater than 40%.* Furthermore, since the variations in density and in heat capacity are both small (i.e., <7% and <4%, respectively) in the whole range of the particle size under the present study, the effect of increasing particle size on the thermal conductivity is therefore considered to be primarily due to the decrease in the interface surface area between the filler and the matrix. (Note that, as shown in Fig. 7, the specific surface area of the AlN powder which determines the interface area decreases significantly with increasing particle size.).

Among the various models,[10,11,23] the Kanari equation[10,24] is reported to be suitable for prediction of the thermal conductivity of the EMC with nonspherical filler. It can be written as

$$1 - \upsilon = \frac{\lambda_e - \lambda_d}{\lambda_c - \lambda_d}\left(\frac{\lambda_c}{\lambda_e}\right)^{1/(1-x)} \quad (1)$$

where υ is the volume fraction of the filler, λ_e is the thermal conductivity of the composite, λ_d is the thermal conductivity of the filler, λ_c is the thermal conductivity of the matrix, and x is a constant determined by sphericity of the filler. Shown in Figure 8 (dotted line)

*Unpublished studies of the present authors in which AlN powders with different oxygen contents were sintered and the thermal conductivities were measured. However, since the thermal conductivity depends strongly on the microstructure, the effect of the oxygen content was difficult to be obtained precisely.

is the calculated thermal conductivity of the EMC, considering the thermal conductivity to be 250 and 0.2 W/mK for the AlN filler and epoxy matrix, and a numerical value of 3 for x. As can be seen, although a few data points are in good agreement with the calculated values, others have significant deviations from them. This may be due to that the Kanari equation does not consider the particle size effect of the filler which, however, has been shown to have a significant effect on the thermal conductivity of the EMC.

CONCLUSIONS

The EMC specimens filled with particulate AlN synthesized by a SHS method were fabricated and effects of several important parameters on their thermal conductivity were investigated. The specimens fabricated by a method involving the use of a solvent (i.e., acetone) were found to have low thermal conductivities. This was considered to be caused by pore formation in the matrix phase due to evaporation of the solvent during the vacuum drying step. It was thus concluded to be essential to densify the matrix phase to obtain a high thermal conductivity of the EMC. The results of the present study also show that the thermal conductivity of the EMC can be significantly increased by coating the AlN particles with silane, which enhances the bonding between the AlN filler and the resin matrix, thus reducing the thermal conduction resistance at the interfaces. Use of AlN powder with large sizes also increased significantly the thermal conductivity of the EMC and this was explained by reduction of the amount of interface which is believed to possess a great thermal conduction resistance. A thermal conductivity of 14 W/mK was achieved under the conditions that a silane-coated AlN powder with a mean particle size of 35.3μm and a filler content of 67 vol % were used and the EMC specimens were fabricated by a process without the use of a solvent.

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